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| (54) Title: NOVEL PROCESSABLE THIOPHENE BASED POLYMERS AND COPOLYMERS AND THERMALLY STABLE ELECTRICALLY CONDUCTING COMPOSITIONS THEREOF (57) Abstract This invention relates to novel processable polymers and copolymers based on recurring thiophene units, and thermally stable electrically conducting compositions made thereof. The invention relates further to processes for the production of said polymers and copolymers as well as to novel substances useful as starting materials in said processes. | | |

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NOVEL PROCESSABLE THIOPHENE BASED POLYMERS AND COPOLYMERS AND
THERMALLY STABLE ELECTRICALLY CONDUCTING COMPOSITIONS THEREOF

This invention relates to novel processable polymers and
5 copolymers based on recurring thiophene units, and thermally
stable electrically conducting compositions made thereof. The
invention relates further to processes for the production of
said polymers and copolymers as well as to novel substances
useful as starting materials in said processes.

10 Polythiophene is considered to be an attractive conducting
polymer because of its improved stability, both in the doped,
or oxidized, and non-doped, or reduced state in comparison
with, for example polyacetylene. Disclosure of polythiophene,
15 both methods for making and use, can be found in numerous
publications and patents. Yamamoto, T., et al., Bull. Chem.
Soc. Jpn. 56, (1983) 1497 - 1502; Tourillon, G., et al., J.
Electroanal. Chem., 135, (1982), 173.

20 One of the major drawbacks of polythiophene is that this
polymer is not processable by common economical means; it does
not dissolve in common solvents nor does it melt or soften at
temperatures below its decomposition temperature.

25 It is well known in the art, that polythiophene can be made
both solution and melt-processable by introduction of long
chain substituents at the 3-position of the thiophene ring.
Thus, for instance, poly(3-alkylthiophene), P3AT, is found to
be soluble in common organic solvents if the alkyl side-chain
30 consists of four carbon atoms (e.g. butyl) or more. Melt-
processability is commonly observed in P2AT when the alkyl
side chain consists of at least six carbon atoms (e.g. hexyl)
or more preferably of at least eight carbon atoms (octyl). The
softening or melting temperature of P3AT decreases with
35 increasing number of carbon atoms in the side-chain. European
Pat. Appl 0 203 438, (1986) (Allied Corporation); Jen, K. Y.,
et al. "Highly conducting soluble and environmentally stable
poly(3-alkylthiophenes)", J. Chem. Soc., Chem. Commun.,
(1986), 1346 - 1347; Sato, M., et al., "Soluble conducting
40 polythiophenes", J. Chem. Soc., Chem.

Commun., (1986), 873 - 874.

It is also known in the art that solution and/or melt-processable P3AT's conveniently can be blended with common thermoplastics polymers, such as polyolefines, polystyrene, polyvinylchloride, polycarbonate, acrylonitrile butadiene styrene (ABS) copolymers an the like. The resulting polymer blends become electrically conducting after treatment with electron accepting agents in the following also called "dopants" or "doping agents", such as Lewis acids, halogens, sulphonic acids and the like. It is believed that this new class of electrically conducting polymer blends will be more cost competitive, easier to process and exhibit superior mechanical and electrical properties as compared to traditional, filled electrically conducting plastics containing carbon black or metal fillers in the form of powders, flakes or fibres. Reference is made to Finnish Patent No 82702.

It is, furthermore, known in the art that a remaining drawback of utilizing P3AT in many practical applications is their insufficient thermal stability in the conducting (oxidized) state. This instability stems from the fact, that the high density of side-chains in homopolymers of P3AT makes it sterically difficult for the dopant molecule to be in close proximity to the conjugated backbone, thereby facilitating the necessary charge-transfer between the conjugated polymer backbone and the dopant agent or compound. This is especially true at high temperatures, where the thermal motions of the side-chains become significant. At these elevated temperatures the free volume available for the dopant is significantly reduced. Furthermore, polymerization of, e.g., 3-octylthiophene commonly leads to an stereo-irregular polymer with ca. 30 - 40 % of head-to-head and tail-to-tail coupling. This situation leads to a non-planar conjugated polymer backbone, due to strong repulsive forces between adjacent side-chains, which results in a poor electron delocalization, and consequently to reduced electrical conductivity. Gustafsson, G., et al. in "Conjugated Polymers", J. L. Brédas

and R. Silbey (eds.), 315 - 362, Kluwer Academic Publishers (1991).

EP 261837 discloses certain electrically conducting bi- and ter-thiophene polymers in which the thiophene units can be substituted. As substituents are mentioned alkyl and alkoxy, but these substituents are expressly lower alkyl or alkoxy of no more than 4 carbon atoms. These polymers have therefore very likely rather low processability.

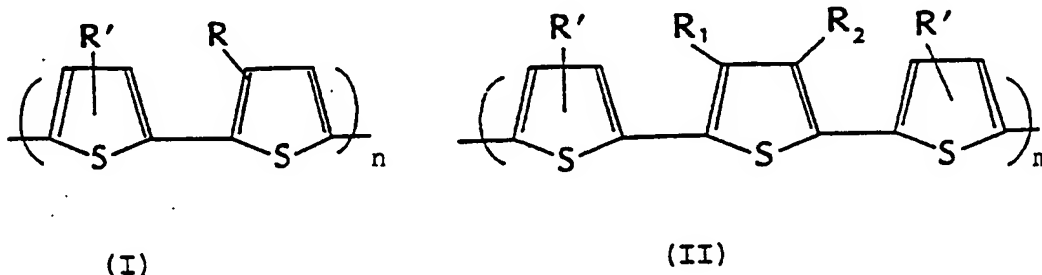
Clearly, a need exists for new processable polythiophene polymers the compositions of which would be of significantly improved thermal stability.

An object of the present invention is to provide novel processable polymers and copolymers based on recurring thiophene units and methods and starting materials for preparing the same.

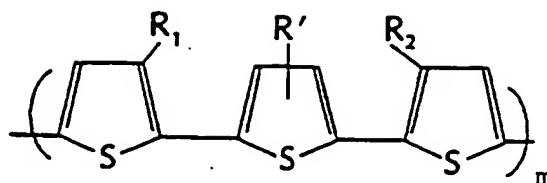
Another object of the invention is to provide novel electrically conducting compositions of significantly improved thermal stability.

Yet another object of the present invention is to provide electrically conductive articles such as shaped articles, fibers, coatings, films, tapes, and the like based on the novel electrically conductive composition.

The invention concerns novel polymer or co-polymer comprising one or more of the mers disclosed in formula I to III



5



(III)

10

wherein R is alkyl, alkenyl, alkoxy, alkanoyl, alkylthio, alkylthioalkyl of 5 to about 30 carbon atoms; or alkylaryl, arylalkyl, alkylsulfinyl, alkoxyalkyl, alkylsulfonyl, alkoxycarbonyl, carboxylic acid where the alkyl or alkoxy group has 1 to about 30 carbon atoms;

R' is hydrogen or a methyl group in the 3- or 4-position of the thiophene ring;

R₁ is hydrogen, alkyl, alkenyl, alkoxy, alkanoyl, alkylthio, alkylthioalkyl of 5 to about 30 carbon atoms; or alkylaryl, arylalkyl, alkylsulfinyl, alkoxyalkyl, alkylsulfonyl, alkoxycarbonyl, carboxylic acid where the alkyl or alkoxy group has 1 to about 30 carbon atoms;

25

R₂ is the same as R₁ except that they cannot simultaneously be hydrogen; or different at each occurrence and is hydrogen, alkyl, alkenyl, alkoxy, alkanoyl, alkylthio, alkylthioalkyl of 5 to about 30 carbon atoms; or alkylaryl, arylalkyl, alkylsulfinyl, alkoxyalkyl, alkylsulfonyl, alkoxycarbonyl, carboxylic acid where the alkyl or alkoxy group has 1 to about 30 carbon atoms;

n is an integer being at least 5 for polymers comprising mers represented by formula I only; and m is an integer being at least 3 for polymers comprising mers represented by either formula II or Formula III or copolymers comprising mers represented by both of the formulas II and III; and for copolymers comprising mers represented by both formula

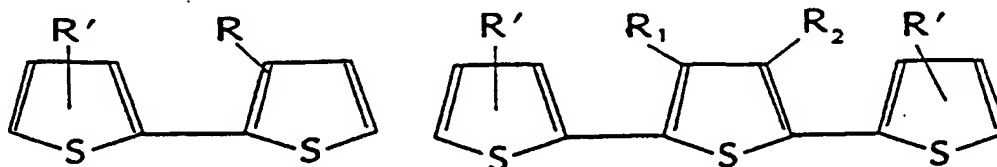
I and one or both of formulas II and III n and m are integers of values great enough to give at least 10 thiophene units in such a copolymer.

5 In the formulas I to III above, the side-chain substitution has been tailored so as to minimize the competition for space between the electron accepting agent or compound and the flexible side-chains.

10 Preferred embodiments of the invention are the polymers of formula I where R is alkyl or alkoxy of 5 to about 30 carbon atoms and n is 5 or greater. If R' is methyl, the methyl group is preferably attached to the 4-position of the thiophene ring.

15 Particularly preferred are the polymers of formula I where R is alkyl of 5 to about 30 carbon atoms and n is 5 or greater. Most preferable are the polymers of formula I where R is alkyl of 6 to about 10 carbon atoms, particularly octyl, and n is 10 or greater.

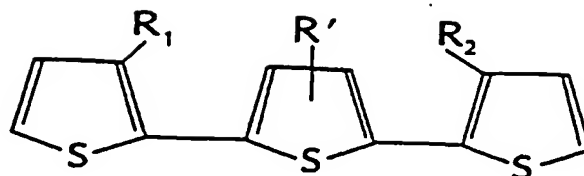
20 The invention includes moreover a process for the preparation of a polymer or a copolymer as defined above where as starting material is used one or more of of the substances IV to VI



(IV)

(V)

5



(VI)

10 wherein R, R', R₁ and R₂ are the same as defined above.

The polymers and copolymers are made from these substances according to chemical or electrochemical polymerization techniques known in the art, for example Gustafson G., et al.
15 "Conjugated Polymers", J L Bredas and R Silbey (eds). Kluwer Academic Publishers (1991), 315-362.

The invention further relates to a novel group of electrically conducting compositions based on a thiophene-units comprising component and an electron accepting agent. In the following
20 "thiophene-units comprising component" shall mean a polymer or copolymer according to this invention as defined above or a mixture of such polymers and/or copolymers. The composition according to this invention exhibit a significant improvement
25 in termal stability properties over compositions known in the art. This superiority results from tailoring the side chain configuration in such a way as to minimize the competition for space between the dopant agent or compound and the flexible side chains.

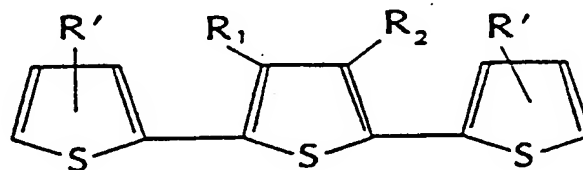
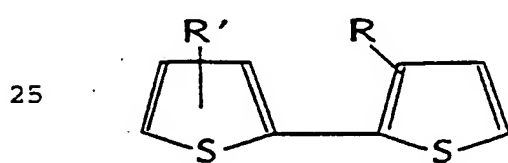
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The electron accepting agent, which can be a single compound or a mixture of several compounds, that form a charge-transfer complex, and thereby impart electrical conductivity with the composition, is selected from the group consisting of metal
35 halides, transition metal halides, halogens and protonic acids. The electrically conducting composition of the invention may optionally furthermore comprise one or more organic substrate phases.

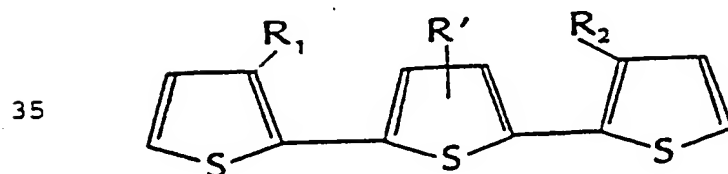
The substrate is an insulating or semiconducting material and can be a bulk oligomeric or polymeric or pre-polymeric material which can be transformed into a fluid form during processing, either in solution, semisolid or melt, so as to achieve required intimate mixing with the thiophene-units comprising component and the electron accepting agent.

Illustrative of useful polymeric substrates are polyethylenes, isotactic polypropylene, elastomers, styrene-butadiene-styrene (SBS) copolymers, polybutadiene, ethylene vinyl acetate copolymers, ethylene butyl acrylate copolymers and the like; poly(vinylchloride), polystyrene, poly(vinylalcohol), poly(ethylene terephthalate), nylons, such as nylon 6, nylon 6.6, and nylon 12 and the like; poly(methylmethacrylate), polycarbonate, acrylonitrile butene styrene copolymers (ABS), and the like.

The invention further relates to certain novel substances useful as starting materials in the preparation of the novel polymers and copolymers of the invention. The novel substances have the formula IV to VI



30



(VI)

wherein R is alkyl, alkenyl, alkoxy, alkanoyl, alkylthio, alkylthioalkyl of 5 to about 30 carbon atoms; or alkylaryl, arylalkyl, alkylsulfinyl, alkoxyalkyl, alkylsulfonyl, alkoxycarbonyl, carboxylic acid where the alkyl or alkoxy group has 1 to about 30 carbon atoms;

R' is hydrogen or a methyl group in the 3- or 4-position of the thiophene ring;

R₁ is hydrogen, alkyl, alkenyl, alkoxy, alkanoyl, alkylthio, alkylthioalkyl of 5 to about 30 carbon atoms; or alkylaryl, arylalkyl, alkylsulfinyl, alkoxyalkyl, alkylsulfonyl, alkoxycarbonyl, carboxylic acid where the alkyl or alkoxy group has 1 to about 30 carbon atoms;

15

R₂ is the same as R₁ except that they cannot simultaneously be hydrogen; or different at each occurrence and is hydrogen, alkyl, alkenyl, alkoxy, alkanoyl, alkylthio, alkylthioalkyl of 5 to about 30 carbon atoms; or alkylaryl, arylalkyl, alkylsulfinyl, alkoxyalkyl, alkylsulfonyl, alkoxycarbonyl, carboxylic acid where the alkyl or alkoxy group has 1 to about 30 carbon atoms.

The substances of formulas IV to VI can be prepared according to the methods described in Examples A and B below, see Gronowitz et al., Heterocycles, 30, (1990), 645.

Overall Compositions

The proportions of materials of the present invention are not very critical and can vary widely, depending on the desired level of electrical conductivity and the application. Generally, higher contents of the conductive polymer or copolymer charge-transfer complex are required to impart higher conductivity to the composition. The relationship between conductivity and amount of dopant: amount of polymer for this invention is the same as for polythiophenes known in the art, see for example Österholm et al., "Synthesis and properties of FeCl₄-doped polythiophene", Synthetic Metals,

18, (1987) 213-218.

Typically, the composition of this invention include polymers or copolymers of this invention as described above or their
5 mixtures (= thiophene-units comprising component"), one or more electron accepting agent or compound and an optional substrate phase. The relative proportions of these materials can range as follows.

10 Thiophene-units
comprising component 1 part by weight

Electron accepting
agent(s) or compound(s) From at least 1 electron accepting
15 agent or compound for each 10
thiophene repeat units, preferably
at least 1 electron accepting agent
or compound for each 5 thiophene
repeat units and most preferable at
20 least 1 electron accepting agent or
compound for each 2 - 3 thiophene
repeat units; typically from 0,01-50
mole-%

25 Substrate 1 part to 100 parts, especially 2 to
500 parts.

In addition to the thiophene-units comprising component, one or more electron accepting agents or compounds and substrates,
30 the compositions used in this invention can include other optional ingredients which either dissolve or do not dissolve in the composition. The nature of such optional ingredients can vary widely, and include those materials which are known to those of skill in the art for inclusion in polymer
35 articles. The total of other materials that can be present is as much as 98 % of the total mixture, and being optional can be omitted altogether. Usually, for commercially attractive products these added ingredients may make up 2 % to 90 % by weight of the total final product.

The method of forming the electrically conductive composition of this invention is not very critical and can vary widely. It is important, however, that at some stage the substrate be
5 processed with the thiophene-units comprising component in a fluid (liquid, semisolid, or molten) form to assure proper intimate mixture. Otherwise, no special requirements are needed and common solution and melt processing techniques known to those ordinarily skilled in the art of polymer
10 processing can be applied, such as solution casting, solution spinning, gel spinning, extrusion, kneading and the like.

Common manufacturing methods may be used to fabricate useful electrically conductive articles from the compositions of the
15 present invention. It will be appreciated by those skilled in the art of polymer product manufacturing that a variety of technologies may be utilized, depending on the nature and shape of the desired article or product.

20 Figure 1 shows the electrical conductivity versus time at 100 °C in dynamic vacuum of poly(3-octyl-2,2'-bithiophene) (PTOT) and poly (3-octyl-co-methylthiophene) (POTMT) of the present invention compared to homopolymer of poly(3-octylthiophene) (P3OT).

25 The following specific examples are presented to illustrate the present invention and are not to be construed as limitations thereon.

30 Example A

This example describes, generally, a useful synthesis route for obtaining substances of formula IV. More particularly the example describes the synthesis route for obtaining 3-alkyl-
35 2,2'-bithiophene.

2-bromo-3-octylthiophene was prepared according to Mitchell et.al, J. Org. Chem, 44, (1979), 4733 and 2-thiopheneboronic acid according to Hörnfeldt et al., Arkiv Kemi, 21, (1963),

249. 3-alkyl-2,2'-bithiophene (Formula IV) was prepared according to Gronowitz et al., Heterocycles, 30, (1990), 645 in which a mixture of 2-bromo-3-alkylthiophene (50 mmol), tetrakis(triphenylphosphine)-palladium(0) (1.5 mmol, 1.736 g) and 1,2-dimethoxyethane (200 ml) was stirred for 10 min. 2-thiopheneboronic acid (60 mmol, 7.708 g) was added immediately followed by sodium bicarbonate (1 M, 150 ml) and the reaction mixture was refluxed for 4 hrs, with vigorous stirring under argon. The organic solvent was evaporated and water (400 ml) and pentane (200 ml) was added to the residue. The mixture was filtered and separated. The water phase was extracted with pentane (3 x 100 ml) and the combined pentane phases were washed with water (100 ml) and brine (50 ml), dried over sodium sulphate. The pentane solution was evaporated and the crude product (13.85 g, purity 78 %) was distilled at 120 - 130 °C to yield 3-alkyl-2,2'-bithiophene in 67 % yield and 94 % purity.

Example B

This example describes, generally, a viable synthesis route for obtaining substances of formula V or VI. More particularly, the example describes the synthesis route for obtaining alkyl-substituted substances of formula V or VI.

The substances of formula V were synthesized according to Example A, with the exception that instead of 2-bromo-3-alkylthiophene, 2,5-dibromo-3-alkylthiophene and 2,5-dibromo-3,4-dialkylthiophene, respectively, were reacted with 2-thiopheneboronic acid.

The substances of formula VI were synthesized according to Example A, with the exception that instead of 2-bromo-3-alkylthiophene, 2,5-dibromothiophene were reacted with 3-alkyl-2-thiophene boronic acid.

Example 1

This example describes, generally a useful synthesis route for

obtaining polymers of structures as shown in formula I, II and III by polymerization of thiophene-based substances of structures as shown in Formula IV, V and VI.

5 A slurry of anhydrous ferric chloride (7.2 mmol, 1,2 g) and chloroform (16 ml) was stirred under argon at room temperature for 10 min. The slurry was added dropwise with a syringe to a solution of 3-octyl-2,2'-bithiophene (1.8 mmol, 0.509 g, GC
10 purity 94 %) and chloroform (6 ml) under argon, stirred on ice bath for 2,5 hrs. Methanol (150 ml) was added and a precipitate was formed which was filtered off and washed with methanol (300 ml). The precipitate, chloroform (75 ml) and concentrated ammonia (75 ml) was stirred under heating for 15
15 minutes. The ammonia phase was separated and new ammonia (75 ml) was added. This was repeated four times. The chloroform phase was washed with a solution of EDTA (75 ml) under stirring and heating, two times. The chloroform phase was filtered and the chloroform evaporated. The polymer so
20 obtained, was dissolved in chloroform (8 ml) and methanol (150 ml) was added. No precipitate was formed over night. The solvent was evaporated until a residue of approximately 10 ml was left. A precipitate was formed and was filtered off and washed with methanol (500 ml). The precipitate was dried to
25 yield poly(3-octyl-2,2'-bithiophene) (0.436g, 86 %). The weight average molecular weight, Mw, was 17000 and the absorption maximum of a chloroform solution of the polymer was 464 nm (UV).

Example 2

30

A polymer of the structure as shown in Formula II, where R₁ and R' are hydrogen and R₂ is octyl, was prepared according to example 1, using as starting material a substance of formula V
35 where R₁ and R' are hydrogen and R₂ is octyl. The polymer was soluble in chloroform.

Example 3

A polymer of the structure as shown in Formula III, where R' is hydrogen, R₁ is octyl and R₂ is octyl, was prepared according to example 1 using as starting material a substance of formula VI where R' is hydrogen and R₁ and R₂ both are octyl. The polymer was soluble in chloroform.

Example 4

10

1 g of poly(3-octyl-2,2'-bithiophene), made according to example 1, was dissolved in acetonitrile. The resulting solution was poured onto a glass plate and, subsequently, the acetonitrile was evaporated. The polymer film formed, was immersed in a

15

0.05 M solution of anhydrous FeCl₃ for one hour. The as-produced FeCl₃-doped poly(3-octyl-2,2'-bithiophene) had an electrical conductivity of 3.4 S/cm as measured by the four point technique.

20

Example 5

A film of FeCl₃-doped poly(3-octyl-2,2'-bithiophene), having a conductivity of 2.6 S/cm, was exposed to a temperature of 110 °C for one hour under dynamic vacuum. The conductivity after one hour at 110 °C was 1.8 S/cm.

25

Example 6

A film of FeCl₃-doped poly(3-octylthiophene), having a conductivity of 8.7 S/cm, was exposed to a temperature of 110 °C for one hour under dynamic vacuum. The conductivity of the film after one hour at 110 °C was 7×10^{-5} S/cm.

30

Examples 5 and 6 demonstrate, that by making compositions of polymers of Formula I, II and III, in which the side-chain configuration is tailored so as to minimize the competition for space between the dopant agent or compound and the flexible side-chain, compositions are produced that exhibit

35

superior thermal stability properties over known compositions based on homo- and random co-polymers of substituted polythiophenes or co-polymers of substituted and/or unsubstituted polythiophenes and/or mixtures thereof, while retaining the desirable processability properties. Reference is made to Figure 1.

Example 7

100 mg of a polymer sample of the structure of Formula 3, where R_1 is methyl and R_2 is octyl, e.g. poly(3-methyl-co-octyl thiophene), was compression molded at 180 °C for 1 minute. The sample melted and the uniform, flexible film, after being doped with $FeCl_3$ according to example Example 4, had an electrical conductivity of 0.9 S/cm. After heating the sample at 110 °C for one hour the conductivity was 0.76 S/cm.

This example demonstrate, that melt-processable compositions can be produced using polymers of Formula I, II and III, while retaining the excellent thermal stability properties as compared to known compositions based on homo- and random co-polymers of substituted polythiophenes or co-polymers of substituted and/or unsubstituted polythiophenes and/or mixtures thereof. Reference is made to Figure 1.

Example 8

100 mg of poly(3-octyl-2,2'-bithiophene) and 1 g of low density polyethylene (LDPE) were co-dissolved in hot toluene (or xylene) and intimately mixed. The resulting red solution was spread onto a glass plate and the solvent evaporated. The resulting film of the blend was tough and flexible and had a conductivity of 3×10^{-2} S/cm after doping according to Example 4.

This example demonstrate, that compositions of polymers of structures as shown in Formula I - III can be solution processed with common, insulating polymers to form electrically conducting polymer blends with excellent

mechanical and electrical properties.

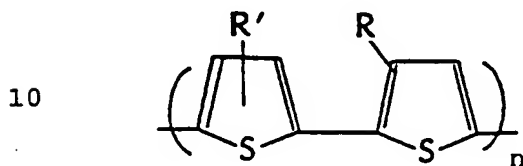
Example 9

5 100 mg of finely divided powder of poly(3-octyl-2,2'-
bithiophene) and 1 g of finely divided LDPE powder were mixed
in a mortar. The mixture was compression molded at 180 °C for
5 minutes to form a uniform blend. After doping according to
example 4, the though, flexible blend film had a conductivity
10 of 3.4×10^{-3} S/cm.

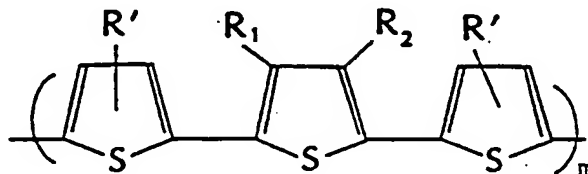
This example demonstrate, that compositions of polymers of the
structures as shown in Formula I - III, can be melt-blended
with common, insulating polymers to form conducting polymer
15 blends with excellent electrical and mechanical properties.

CLAIMS

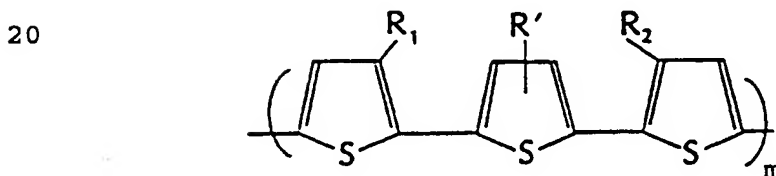
1. A novel polymer or copolymer based on recurring thiophene units characterized in that it comprises one or more of the mers represented by the groups within the parentheses in formula I to III



(I)



(II)



(III)

25

wherein R is alkyl, alkenyl, alkoxy, alkanoyl, alkylthio, alkylthioalkyl of 5 to about 30 carbon atoms; or alkylaryl, arylalkyl, alkylsulfinyl, alkoxyalkyl, alkylsulfonyl, alkoxy carbonyl, carboxylic acid where the alkyl or alkoxy group has 1 to about 30 carbon atoms;

30

R' is hydrogen or a methyl group in the 3- or 4-position of the thiophene ring;

35

R₁ is hydrogen, alkyl, alkenyl, alkoxy, alkanoyl, alkylthio, alkylthioalkyl of 5 to about 30 carbon atoms; or alkylaryl, arylalkyl, alkylsulfinyl, alkoxyalkyl, alkylsulfonyl,

alkoxycarbonyl, carboxylic acid where the alkyl or alkoxy group has 1 to about 30 carbon atoms;

5 R₂ is the same as R₁ except that they cannot simultaneously be be hydrogen; or different at each occurrence and is hydrogen, alkyl, alkenyl, alkoxy, alkanoyl, alkylthio, alkylthioalkyl of 5 to about 30 carbon atoms; or alkylaryl, arylalkyl, alkylsulfinyl, alkoxyalkyl, alkylsulfonyl, alkoxycarbonyl, carboxylic acid where the alkyl or alkoxy group has 1 to about
10 30 carbon atoms;

n is an integer being at least 5 for polymers comprising mers represented by formula I only; and m is an integer being at least 3 for polymers comprising mers represented by either
15 formula II or Formula III or copolymers comprising mers represented by both formulas II and III; and for copolymers comprising mers represented by both formula I and one or both of formulas II and III n and m are integers of values great enough to give at least 10 thiophene units in
20 such a copolymer.

2. A polymer according to claim 1 c h a r a c t e r i z e d in that it has the structure of formula I where R is alkyl or alkoxy of 5 to about 30 carbon atoms and n is 5 or greater.
25

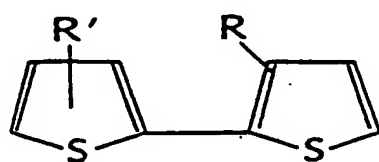
3. A polymer according to claim 2 c h a r a c t e r i z e d in that R is alkyl of 5 to about 30 carbon atoms and n is 5 or greater.

30 4. A polymer according to claim 3 c h a r a c t e r i z e d in that R is alkyl of 6 to 10 carbon atoms and n is 10 or greater.

35 5. A polymer according to claim 4 c h a r a c t e r i z e d in that R is octyl.

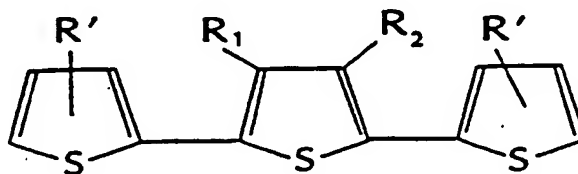
6. A process for the preparation of a polymer or a copolymer as defined in any of the claims 1 to 5 according to known methods characterized in that as starting material is used one or more of the substances IV to VI

5



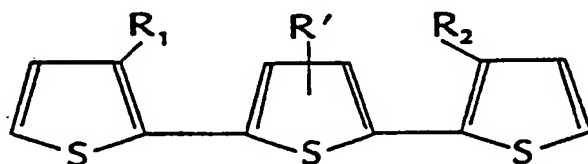
(IV)

10



(V)

15



20

(VI)

wherein R, R', R₁ and R₂ are the same as defined in claim 1.

25

7. A process according to claim 6 characterized in that a substance of formula IV is used as starting material to give a polymer of formula I.

30

8. A process according to claim 6 characterized in that a substance of formula V is used as starting material to give a polymer of formula II.

35

9. A process according to claim 6 characterized in that a substance of formula VI is used as starting material to give a polymer of formula III.

10. An electrically conducting composition based on a thiophene-units comprising component and an electron accepting agent characterized in that said thiophene-units

comprising component is a polymer or copolymer according to any of the claims 1 to 5 or a mixture of such polymers and/or copolymers.

5 11. An electrically conducting composition according to claim
10 c h a r a c t e r i z e d in that the electron accepting
agent, which can be one single compound or a mixture of
compounds, is selected from the group consisting of metal
halides, transition metal halides, halogens and protonic
10 acids.

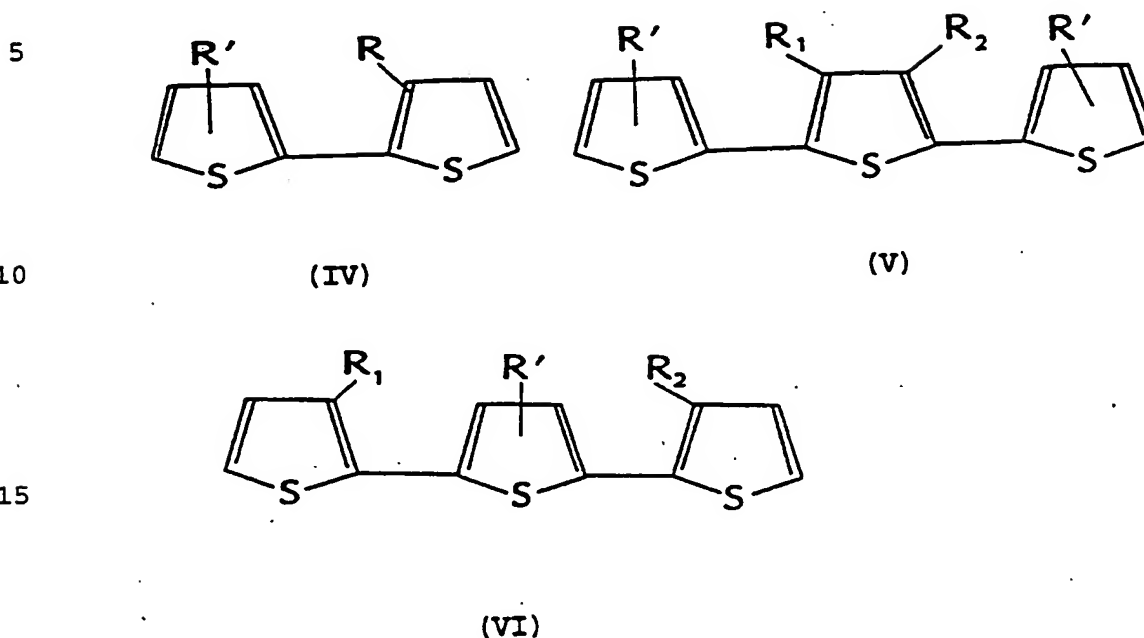
12. An electrically conducting composition according to claim
10 or 11 c h a r a c t e r i z e d in that it comprises a
sufficient amount of a suitable electron accepting agent to
15 give a conductivity of at least 10^{-6} S/cm for said
composition.

13. An electrically conducting composition according to claims
10, 11 or 12 c h a r a c t e r i z e d in that it
20 furthermore comprises one or more organic substrate phases,
said substrate being a bulk oligomeric or polymeric or pre-
polymeric material which can be transformed into a fluid form
during processing, so as to achieve required intimate mixing
with the thiophene-units comprising component and the electron
25 accepting agent.

14. An electrically conducting composition according to claim
13 c h a r a c t e r i z e d in that it comprises a
sufficient amount of a suitable electron accepting agent that
30 imparts to the composition a conductivity of at least 10^{-8}
S/cm.

15. Electrically conducting articles such as static discharge
(SD) electrostatic dissipation (ESD), electromagnetic
35 shielding (EMI), sensors batteries, switches, heating
elements, integrated circuits, microelectronics and
photovoltaics c h a r a c t e r i z e d in that they
comprise a composition according to any of the claims 10 to
14.

16. Novel substances characterized in the formula IV to VI



20

wherein R is alkyl, alkenyl, alkoxy, alkanoyl, alkylthio, alkylthioalkyl of 5 to about 30 carbon atoms; or alkylaryl, arylalkyl, alkylsulfinyl, alkoxyalkyl, alkylsulfonyl, alkoxy carbonyl, carboxylic acid where the alkyl or alkoxy group has 1 to about 30 carbon atoms;

25

R' is hydrogen or a methyl group in the 3- or 4-position of the thiophene ring;

30

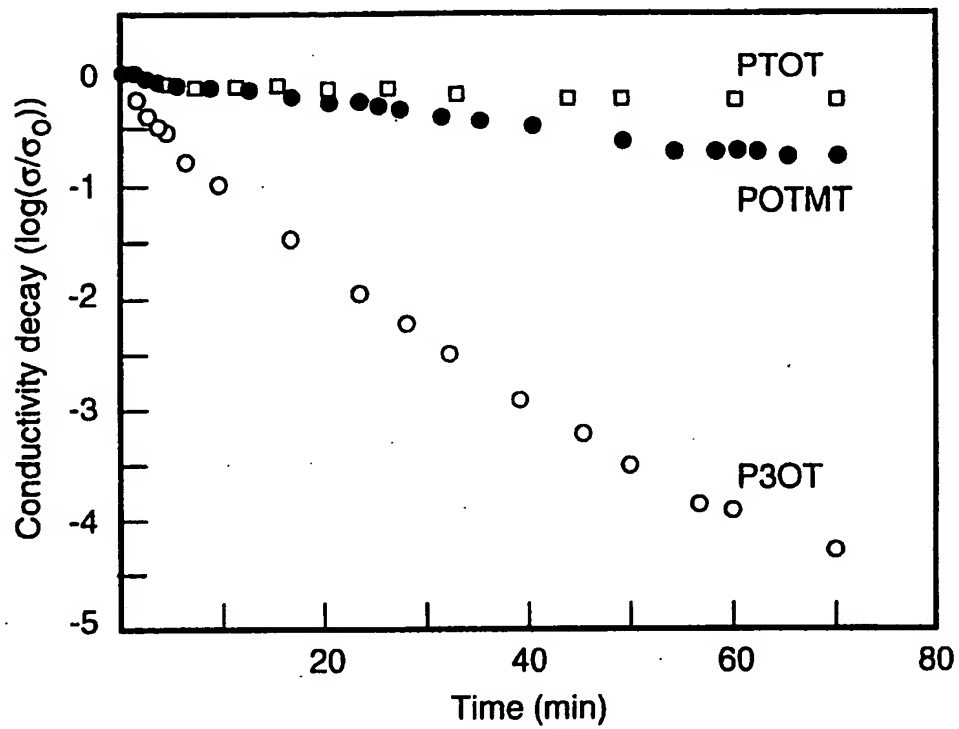
R₁ is hydrogen, alkyl, alkenyl, alkoxy, alkanoyl, alkylthio, alkylthioalkyl of 5 to about 30 carbon atoms; or alkylaryl, arylalkyl, alkylsulfinyl, alkoxyalkyl, alkylsulfonyl, alkoxy carbonyl, carboxylic acid where the alkyl or alkoxy group has 1 to about 30 carbon atoms;

35

R₂ is the same as R₁ except that they cannot simultaneously be be hydrogen; or different at each occurrence and is hydrogen, alkyl, alkenyl, alkoxy, alkanoyl, alkylthio, alkylthioalkyl of 5 to about 30 carbon atoms; or alkylaryl, arylalkyl,

alkylsulfinyl, alkoxyalkyl, alkylsulfonyl, alkoxycarbonyl, carboxylic acid where the alkyl or alkoxy group has 1 to about 30 carbon atoms.

1/1



INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 93/00301

A. CLASSIFICATION OF SUBJECT MATTER

IPC5: C08G 61/12, H01B 1/12, C07D 333/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC5: C08G, H01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI, CA, EDOC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|-----------|---|-----------------------|
| X | EP, A2, 0416567 (HOECHST AKTIENGESELLSCHAFT), 13 March 1991 (13.03.91), abstract, claims -- | 1-16 |
| X | EP, A2, 0261837 (SANYO ELECTRIC CO., LTD.), 30 March 1988 (30.03.88), page 5, line 37; page 6, line 8; page 6, line 31 - line 36, claim 7 -- | 1,6-16 |
| X | EP, A1, 0203438 (ALLIED CORPORATION), 3 December 1986 (03.12.86), column 7, line 19 - line 37, examples, claims -- | 1-16 |

☒ Further documents are listed in the continuation of Box C.
 ☒ See patent family annex.

* Special categories of cited documents:

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

9 November 1993

Date of mailing of the international search report

10 - 11 - 1993

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 93/00301

| C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT | | |
|---|--|-----------------------|
| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
| X | <p>Chemical Abstracts, Volume 113, No 12, 17 Sept 1990 (17.09.90), (Columbus, Ohio, USA), Zagorska, Malgorzata et al, "Chemical synthesis and characterization of soluble poly(4,4'dialkyl-2, 2'-bithiophenes)", page 7, THE ABSTRACT No 98128x, Polymer 1990, 31 (7), 1379-1383</p> <p>-- -----</p> | 1-16 |

INTERNATIONAL SEARCH REPORT
Information on patent family members

01/10/93

International application No.
PCT/FI 93/00301

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
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| EP-A2- 0261837 | 30/03/88 | JP-A- 63069823 US-A- 4795687 JP-A- 63069824 JP-A- 63072069 JP-A- 63072070 JP-A- 63097626 | 29/03/88 03/01/89 29/03/88 01/04/88 01/04/88 28/04/88 |
| EP-A1- 0203438 | 03/12/86 | CA-A- 1284398 JP-A- 61278526 US-A- 4711742 | 21/05/91 09/12/86 08/12/87 |